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Seasonal variations of atmospheric C₂–C₇ nonmethane hydrocarbons in Tokyo

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[1] Eighteen C₂–C₇ NMHCs (nonmethane hydrocarbons) were measured hourly during the Integrated Measurement Program for Aerosol and Oxidant Chemistry in Tokyo (IMPACT) measurement campaigns conducted in central Tokyo during four different periods (summer/autumn of 2003 and winter/summer of 2004). The ambient atmospheric concentrations of NMHCs showed an inverse correlation with wind speed and mixing height and were significantly affected by mesoscale weather conditions. The mixing ratio of isoprene tightly correlated with solar flux and temperature in summer, as it was dominantly emitted by the local vegetation. All the observed NMHCs except isoprene showed high correlation with each other in winter ($r^2 > 0.5$), suggesting concurrent accumulation under stagnant condition and common sources. Emission ratios were calculated on the basis of the correlation with carbon monoxide and ethyne. Compared to the typical winter NMHC composition, during summer there was a significant increase (up to 7 times higher than wintertime) of C₄–C₅ alkanes from fuel evaporation; of C₂–C₃ alkenes, *n*-hexane and benzene from chemical industry; and of toluene from local manufacturers, reflecting the temperature dependence of these evaporative emissions. In addition to the online measurements in Tokyo, canister sampling at a suburban site (Kisai) followed by multidimensional GC analyses was conducted during the summer campaign in 2004. The atmospheric concentrations of longer-lived compounds (\geq several days) at Kisai showed the buildup under sea breeze circulation. The average ambient concentration of toluene was 2 times higher than that in central Tokyo, likely because of substantial emissions from local industries as reported in the prefectural statistics.

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1. Introduction

[2] Together with nitrogen oxides (NO_x), nonmethane hydrocarbons (NMHCs) are important precursors of photochemical oxidants and suspended particulate matter (SPM) in the atmosphere. In Tokyo, despite the decrease of con-

centrations of these precursors by pollution control efforts, the problem of photo-oxidants still remains one of the major issues of urban air quality. The governmental term “photo-oxidants” stands for photochemical products in the atmosphere, commonly monitored by absorption spectrophotometry using a neutral potassium iodide solution. It mostly consists of ozone (>90%), with minor amount of other species such as peroxyacetyl nitrate (PAN), aldehydes, etc. The annually averaged daytime (0500–2000 local time (LT)) concentration of photo-oxidants in Tokyo increased from 21 ppb to 27 ppb between 1990 and 2002 at the annually averaged increase rate of 0.47 ppb a^{−1}. In addition, the frequency of photochemical oxidant warning days, when the oxidants concentration level stays above hourly averages of 0.12 ppm, has rapidly increased since 2000 and has also spread to a wider area [Tokyo Metropolitan Government Office, 2005]. In Japan, antipollution measures began in the 1960s, starting with controlling industrial smoke and emissions from factories, and promoting the use of high-quality fuels. Exhaust emission control was imposed in the 1970s and has been repeatedly tightened since. The Automobile NO_x Reduction Law went into effect

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in December 1993 and Diesel Vehicle Control has been carried out in Tokyo and its environs since October 2003. The development and adoption of low-emission cars and the improvement of fuels have resulted in a significant reduction in hazardous emissions from automobiles. However, the effect of emission controls is being counteracted by the growing number of vehicles (from 3.4 million vehicles in 1960 to 74 million vehicles in 2004 [Ministry of Land Infrastructure and Transport (MLIT), 2005]), and vehicle exhaust still remains a major source of air pollutants in urban areas. In addition, the recent increase of high photo-oxidant events may be related to the different decrease rate of NO_x and NMHCs. Wakamatsu *et al.* [1996] analyzed the trends of the annual average concentrations of NO_x and NMHCs in the vicinity of Tokyo and Osaka between 1978 and 1990 and found that the NMHC/ NO_x ratio had decreased in the long term in both areas. During that period, the decrease rate was greater for NMHCs than for NO_x . However, since 2000, while the decrease rate of NO_x concentration in urban air quickened as a result of the emission control for automobiles, the rate slowed for NMHCs, which have a wider variety of sources other than automobile exhaust, such as solvent use, chemical industry, and fossil fuel processing/distribution. The production of photo-oxidants depends on both NO_x and NMHCs in urban air, but it is usually NMHC-limited in the center-city sections where enough NO_x is available [Sillman *et al.*, 1990]. Thus, even though the concentration of each pollutant decreased, the recent increase of the NMHC/ NO_x ratio may have enhanced the production rate of photo-oxidants.

[3] Apart from the emission controls for mobile sources, until recently there has been no regulation for NMHCs (except for some toxic air pollutants such as benzene and trichloroethene) in Japan. In 2001, the Pollutant Release and Transfer Register (PRTR) Law took effect, which requires businesses to report the release of chemical substances including a number of NMHCs. The purpose of this law is (1) to promote the businesses' voluntary improvements in the management of specific chemical substances from stationary sources and to prevent any impediment of environmental protection and (2) to provide technical information on the properties and handling of such substances. However, as PRTR is not a regulatory law, the Ministry of the Environment (MOE) decided to introduce guidelines for the regulation of NMHC emissions from stationary sources in the Air Pollution Control Law of May 2005, in response to the low achievement of the environmental standards regarding Suspended Particulate Matter (SPM) and photochemical oxidants. This first full-scale regulation for NMHC emissions in Japan will be in force within the following 2 years.

[4] The ambient level of NMHCs reflects the characteristics of emission patterns from local traffic, energy use, and industrial activities in addition to photochemistry and meteorology. However, despite the increasing number of air monitoring stations along with the environmental controls of national/provincial governments, there are still very limited data published regarding individual NMHCs because most of the public stations only monitor the total amount of atmospheric NMHCs by the procedure specified by the law. There are some literature values from previous observations of light NMHCs in cities in Japan and east

Asia [Guo *et al.*, 2004; Miyoshi and Makide, 2001; Morikawa *et al.*, 1998; Tanaka *et al.*, 1993, 2001b; Tsujino and Kuwata, 1993; Yoshino *et al.*, 2005], but it is difficult to find an up-to-date data set from central Tokyo which is comparable to the recent online NMHCs measurement in cities abroad [Derwent *et al.*, 2000; Durana *et al.*, 2006; Navazo *et al.*, 2002] because of a biased time and season of sampling and/or an obvious strong signature of neighborhood sources. The main goals of this study were to accurately determine the present concentrations and variations of 18 C_2 – C_7 NMHCs in central Tokyo; to elucidate the major factors controlling their variations; to know the typical chemical composition, the source contributions and its seasonal variations in central Tokyo; and to make comparisons with the data in a suburban area. It is also important to measure preregulation air quality in order to later detect the effect of the revised regulations.

2. Experiments

[5] The intensive measurement campaigns of the Integrated Measurement Program for Aerosol and oxidant Chemistry in Tokyo (IMPACT) study have been conducted since 2003 within the framework of “Mega-Cities: Asia as a source of aerosols and oxidants,” one of the tasks of International Global Atmospheric Chemistry (IGAC). The C_2 – C_7 NMHC data sets presented in this study were obtained during the IMPACT campaigns which took place at the Komaba campus of the Research Center for Advanced Science and Technology of the University of Tokyo (35.4°N, 139.4°E) located in the heart of downtown Tokyo (Figure 1). Four intensive campaigns were conducted from 19 July to 13 August and 2–15 October of 2003, and 20 January to 6 February and 26 July to 14 August of 2004. Data sets are called “summer_2003,” “autumn_2003,” “winter_2004,” and “summer_2004,” respectively, in this paper. In addition to NMHC measurements, other compounds and parameters, which focused on the processes of formation, removal, and transport of aerosols, were measured by other groups and have been described elsewhere [Kita *et al.*, 2006; Kondo *et al.*, 2006, 2007; Miyazaki *et al.*, 2006; Mochida *et al.*, 2006; Morino *et al.*, 2006; Takegawa *et al.*, 2005, 2006a, 2006b]. To mention a few, ozone and CO were measured by the absorption of ultraviolet (UV) and infrared (IR), respectively, and meteorological parameters were also measured on site during the campaigns.

[6] The C_2 – C_7 NMHCs were measured by online gas chromatograph (Agilent 6890) with a flame ionization detector (GC-FID) installed in a laboratory on the fifth floor of a five-story building. The 18 NMHCs that were measured include alkanes, alkenes, alkynes, and aromatics (Table 1). Ambient air was drawn via a 3/4 outer diameter Teflon tube from an inlet placed at the rooftop approximately 18 m above the ground. Preconcentration was done prior to the GC analysis with a slightly modified unit of the cryogenic preconcentration system which had been developed for trace halocarbons in the atmosphere. Details about the experimental procedure have been described elsewhere [Enomoto *et al.*, 2005; Yokouchi *et al.*, 2005], but a brief explanation is as follows. For each analysis, 300 mL of air was preconcentrated by two-stage absorbent traps (1: Carboxene 1000 + Carboxene B at -110°C and 2: Carboxene

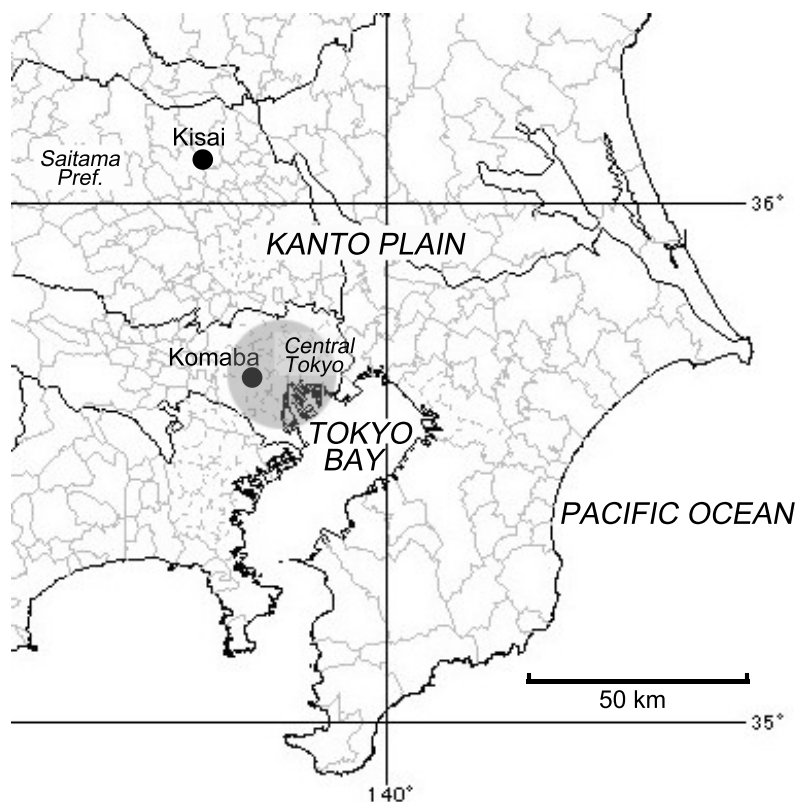


Figure 1. Tokyo Metropolitan Area with the locations of the IMPACT campaign sites (Komaba and Kisai). “Central Tokyo” (the shaded area) refers to the highly urbanized area of Tokyo.

1000+glass beads at -70°C), respectively, using a mechanical cooler after dehumidifying using a Nafion tube. NMHCs were volatilized by thermal desorption and were injected to the analytical column (Alumina PLOT; $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$) of the GC. All the measurements were automated and conducted hourly including one standard run per day. The air sampling occurred during the first 10 min of each 1-h analysis cycle. The standard gas was a mixture of the targeted hydrocarbons in which the concentrations were set at approximately 1 ppbv each, prepared by Taiyo Toyo Sanso Co., Ltd. Reproducibility, which was evaluated by rsd (relative standard deviation) of the measurements of the standard mixture during the experimental period, was less than 1% for most of the measured species, except for C_2H_2 (4.0%), C_3H_6 (1.7%), *cis*-2- C_4H_8 (5.2%), C_5H_8 (19.4%), C_6H_6 (2.9%), and C_7H_8 (3.6%). The detection limit was approximately 4 pptv for propane to achieve a signal-to-noise ratio higher than 3. As mentioned above, 23 samples were generally collected each day during each campaign, and the total number of measured samples during “summer_2003,” “autumn_2003,” “winter_2004,” and “summer_2004” was 429, 274, 342, and 439, respectively.

[7] As part of the summer_2004 IMPACT campaign, simultaneous observations were conducted on the campus of the Center for Environmental Science in Saitama prefecture located in the suburban town of Kisai in the northwest part of the Kanto Plain (Figure 1). The Kanto Plain is the largest plain in Japan (approximately $15,000\text{ km}^2$) and is very flat (the range of elevation is within 50 m above sea level for

most of the area shown in Figure 1), reducing the complexity of local topography. The Kisai observation was aiming to see the evolution of urban emissions in a suburban area that is generally downwind from central Tokyo in the daytime because of the land-sea breeze interchange between Tokyo Bay and the Kanto Plain. Ambient air was collected in clean, evacuated 2-L stainless steel canisters equipped with a bellows valve 4–12 times a day (8 times a day on average) from a balcony of a second-story building at approximately 5 m above ground level. 154 samples in total were taken at Kisai from 26 July to 14 August of which two thirds were collected in the daytime (where “daytime” and “nighttime” were divided at 0700 and 1900 LT). Except for this bias toward daytime sampling, the sampling interval was set as evenly as possible. The filled canisters were sent to the University of California at Irvine and up to 80 VOCs including 44 C_2 – C_{10} hydrocarbons were quantitated using a multidimension GC-FID/ECD/MS system. Detailed descriptions of the analysis and data quality have been presented by Colman *et al.* [2001]. Additionally, 30 canister samples were collected at the Komaba observation site (= the campus of U. Tokyo) during the summer 2004 campaign period and the values were intercompared with those obtained by the online automated GC-FID system of the National Institute for Environmental Studies (NIES) presented in this study. For both canister and online sampling, sampling time was set on the hour and twenty-four cases were chosen for the intercomparison, while the remaining 6 cases could not make pairs because of the coincidence of the

Table 1. Median Mixing Ratios With the 25th and 75th Percentiles, the Minimum and the Maximum of Measured Species at the Komaba Site During Previous Four IMPACT Campaigns^a

Compounds	Formula	Summer_2003			Autumn_2003			Winter_2004			Summer_2004		
		Median	25–75%	Minimum–Maximum	Median	25–75%	Minimum–Maximum	Median	25–75%	Minimum–Maximum	Median	25–75%	Minimum–Maximum
Alkanes													
Ethane	C ₂ H ₆	2.42	1.71–3.98	0.70–91.9	3.06	2.56–3.74	1.03–25.2	5.39	4.34–6.87	0.98–5.39	1.59	1.11–2.37	0.61–7.94
Propane	C ₃ H ₈	2.36	1.46–4.44	0.50–73.1	2.83	2.02–4.40	0.75–27.7	5.14	3.51–7.88	0.99–5.14	1.72	1.18–3.05	0.57–22.7
<i>i</i> -Butane	<i>i</i> -C ₄ H ₁₀	1.31	0.77–2.28	0.29–12.0	1.26	0.82–1.87	0.40–13.7	1.70	1.11–2.64	0.35–1.70	1.13	0.76–1.79	0.35–7.93
<i>n</i> -Butane	<i>n</i> -C ₄ H ₁₀	2.25	1.32–3.68	0.44–15.8	1.97	1.30–2.95	0.62–21.5	2.46	1.65–3.64	0.55–2.46	2.05	1.33–3.49	0.61–15.0
<i>i</i> -Pentane	<i>i</i> -C ₅ H ₁₂	1.51	0.89–2.50	0.24–9.15	1.05	0.76–1.52	0.36–14.0	1.16	0.67–1.79	0.20–1.16	1.67	1.00–2.75	0.35–13.9
<i>n</i> -Pentane	<i>n</i> -C ₅ H ₁₂	0.68	0.39–1.15	0.11–4.34	0.52	0.39–0.78	0.20–6.14	0.58	0.35–0.85	0.15–0.58	0.77	0.45–1.39	0.18–7.30
<i>n</i> -Hexane	<i>n</i> -C ₆ H ₁₄	0.40	0.22–0.72	0.05–3.37	0.45	0.28–0.62	0.09–3.76	0.51	0.29–0.80	0.14–0.51	0.52	0.32–0.76	0.13–2.87
Alkenes													
Ethene	C ₂ H ₄	1.66	1.05–3.67	0.33–43.1	2.06	1.36–2.97	0.45–34.6	3.03	1.84–4.94	0.66–3.03	1.16	0.73–1.98	0.29–23.4
Propene	C ₃ H ₆	0.47	0.31–0.97	0.12–10.3	0.57	0.35–0.79	0.08–11.3	0.76	0.29–1.36	0.02–0.76	0.37	0.23–0.56	0.10–8.53
<i>trans</i> -2-Butene	<i>trans</i> -2-C ₄ H ₈	0.14	0.09–0.21	b.d.l.–0.75	0.11	0.07–0.17	b.d.l.–1.80	0.07	0.00–0.20	b.d.l.–0.07	N/A	N/A	N/A
1-Butene	1-C ₄ H ₈	0.14	0.09–0.26	b.d.l.–1.57	0.12	0.07–0.20	b.d.l.–1.64	0.16	0.02–0.32	b.d.l.–0.16	0.14	0.09–0.22	0.01–2.90
<i>i</i> -Butene	<i>i</i> -C ₄ H ₈	0.21	0.15–0.28	b.d.l.–1.27	0.09	0.04–0.13	b.d.l.–1.42	0.08	0.04–0.14	0.01–0.08	N/A	N/A	N/A
<i>cis</i> -2-Butene	<i>cis</i> -2-C ₄ H ₈	0.11	0.07–0.18	b.d.l.–0.71	0.08	0.04–0.12	b.d.l.–1.50	0.04	0.00–0.14	b.d.l.–0.04	0.13	0.09–0.18	b.d.l.–0.99
Isoprene	C ₅ H ₈	0.11	0.06–0.31	b.d.l.–2.73	0.04	0.03–0.07	0.01–0.86	0.01	0.01–0.02	b.d.l.–0.01	0.09	0.05–0.42	0.01–2.22
1,3-Butadiene	1,3-C ₄ H ₆	N/A	N/A	N/A	N/A	N/A	N/A	0.01	N/A	N/A	0.04	0.03–0.06	0.01–1.34
Alkynes													
Ethyne	C ₂ H ₂	1.01	0.69–1.87	0.19–7.68	1.43	1.13–1.88	0.32–10.2	2.54	1.90–3.52	1.10–2.54	0.75	0.50–1.14	0.19–3.19
Aromatics													
Benzene	C ₆ H ₆	0.30	0.19–0.67	0.04–3.22	0.36	0.27–0.51	0.09–3.10	0.65	0.48–0.90	0.31–0.65	0.18	0.12–0.32	0.05–2.21
Toluene	C ₇ H ₈	1.58	0.96–2.77	b.d.l.–15.0	2.45	1.62–4.55	b.d.l.–16.2	3.17	1.78–5.05	0.60–3.17	1.28	0.79–1.91	0.42–30.5

^a“b.d.l.” denotes “below detection limit.” “N/A” denotes “not available.”

Table 2. Results From a Linear Regression Analysis of Data Measured by NIES and by UCI for Simultaneously Collected Samples at Komaba

Compounds	Slope	r^2
Ethane ^a	0.93	0.96
Ethene ^b	0.88	0.91
Propane ^a	0.92	0.95
Propene ^a	0.82	0.90
<i>i</i> -Butane ^b	0.95	0.96
<i>n</i> -Butane ^a	0.97	0.97
Ethyne ^b	0.83	0.84
1-Butene ^b	0.63	0.42
<i>cis</i> -2-Butene ^b	0.80	0.82
<i>i</i> -Pentane ^a	0.95	0.94
<i>n</i> -Pentane ^a	0.93	0.96
1,3-Butadiene ^a	0.84	0.92
<i>n</i> -Hexane ^b	0.70	0.85
Isoprene ^b	0.40	0.71
Benzene ^a	1.05	0.93
Toluene ^a	1.02	0.93

^aTwo outliers have been eliminated from the original data set.^bOne outlier has been eliminated from the original data set.

canister sampling and the standard run of the online system. Strictly speaking, the sampling takes longer (10 min) for the online system than for the grab sampling (a few minutes), but air masses collected for those two measurements were determined to be identical in the timescale of 10 min. The results of a linear regression analysis performed on the data obtained by NIES and UCI are shown in Table 2. One of two outliers identified by the standardized residuals greater than 2 was eliminated from the original data set (Table 2). The outliers have not been found in particular samples. The outliers of the compounds of the same group (alkanes, alkenes ...) and of similar reactivity tended to be found in the same samples possibly reflecting the age of air in each sample. The maximum standardized residual in the whole data set was 3.3 for propene. The response and the correlation were quite good for most of the measured compounds, except for 1-butene and isoprene which showed considerable discrepancy. The reason for this discrepancy is not clear, but it was possibly affected by either the difference in the chromatogram processing/sampling procedure or the stability of running standard gas. Because of this discrepancy, 1-butene and isoprene were set aside when making comparisons between Komaba and Kisai. For the other compounds which showed good responses, the UCI values were adjusted to NIES calibration by multiplying by the slopes of the regression line shown in Table 2 when used in the following discussions.

3. Results and Discussion

3.1. Seasonal and Diurnal Variations of C₂–C₇ NMHCs in Central Tokyo

[8] The median mixing ratios of the 18 NMHC species measured during each campaign period are shown in Table 1. Ratios of the median values to the winter_2004 values are shown in Table 3. Seasonal and diurnal variations of NMHCs are mostly caused by variations of emission strengths, loss rates, and meteorological conditions (wind speed and direction, mixing height, etc.). In this section, the seasonal and diurnal variations of NMHCs observed in central Tokyo (Komaba site) are described in terms of these

three controlling factors. Further discussion on the typical source profile is given in section 3.2.

3.1.1. Comparison Between Summer 2003 and 2004 Data

[9] It is noted that even for the same season, we can clearly see the difference between the values from “summer_2003” and “summer_2004.” For example, ethane, ethene, and benzene had almost 2 times higher values in summer_2003 than in summer_2004. The considerable difference between these data sets is attributable to the difference in local weather conditions between years. In summer_2003, the rainy season lasted until the beginning of August, whereas it ended early in mid-July in summer_2004. During summer_2003 and summer_2004, the mean temperatures were $25.4 \pm 3.5^\circ\text{C}$ and $28.5 \pm 2.3^\circ\text{C}$, the daytime mean UV-B radiance (from 0600 to 1800 LT) was $0.32 \pm 0.27 \text{ W/m}^2$ and $0.35 \pm 0.35 \text{ W/m}^2$, and the mean relative humidity was $73 \pm 11\%$ and $67 \pm 13\%$, respectively. The average values of many observed NMHCs were considerably elevated in summer_2003 (by 50–90%) because of occasional extremely high levels when crossing the seasonal rainy front (a stationary front called the Baiu or Meiyu front). Under these conditions NMHCs were considered to accumulate within colder side air mass near the surface below the temperature inversion. In contrast, the average values in summer_2004 were biased to lower values by the frequent approach of typhoons during the observation period, which flushed out the stagnated plumes with strong southern wind. To reduce the effect from extreme cases, median values are used instead of average values in this study.

3.1.2. Influences of Emissions and Loss Rates

[10] Similar seasonal patterns of certain species indicate the similarity in their atmospheric lifetime and source profile. The typical OH lifetimes of the measured NMHCs are calculated on the basis of the OH concentration observed at the Komaba site during the IMPACT campaigns [Kanaya *et al.*, 2007] (Table 4). In response to seasonal changes in the abundance of OH, the lifetimes of these species are 4 times longer in winter than in summer. The

Table 3. Ratios of Median Values of Measured Species Normalized by the Winter_2004 Data^a

Compounds	Summer 2003	Autumn 2003	Winter 2004	Summer 2004
Ethane	0.45	0.57	1	0.29
Ethene	0.55	0.68	1	0.38
Ethyne	0.40	0.56	1	0.30
Propane	0.46	0.55	1	0.34
Propene	0.62	0.75	1	0.49
<i>i</i> -Butane	0.77	0.74	1	0.66
<i>n</i> -Butane	0.91	0.80	1	0.83
<i>trans</i> -2-Butene	1.98	1.53	1	N/A
1-Butene	0.89	0.74	1	0.84
<i>i</i> -Butene	2.78	1.15	1	N/A
<i>cis</i> -2-Butene	2.85	2.07	1	3.34
<i>i</i> -Pentane	1.31	0.91	1	1.45
<i>n</i> -Pentane	1.17	0.90	1	1.32
Isoprene	8.72	3.05	1	7.26
<i>n</i> -Hexane	0.79	0.88	1	1.02
Benzene	0.45	0.56	1	0.28
Toluene	0.50	0.77	1	0.40

^aN/A denotes “not available.” 1,3-butadiene is not shown because it was observed only in summer_2004.

Table 4. Tropospheric Lifetimes for Selected NMHCs Based on Mean OH Concentrations Observed in Central Tokyo During the IMPACT Campaign Period [Kanaya *et al.*, 2007]^a

Compounds	Lifetime, Summer	Lifetime, Winter
Ethane	23	96 ^b
Ethene	0.70	2.9 ^b
Ethyne	7.1	30 ^b
Propane	5.0	21 ^b
Propene	0.19	0.80 ^b
<i>i</i> -Butane	2.6	11 ^c
<i>n</i> -Butane	2.4	10 ^b
<i>trans</i> -2-Butene	0.086	0.36 ^d
1-Butene	0.18	0.76 ^c
<i>i</i> -Butene	0.11	0.46 ^f
<i>cis</i> -2-Butene	0.10	0.41 ^d
1,3-Butadiene	0.083	0.35 ^d
<i>i</i> -Pentane	1.5	6.4 ^g
<i>n</i> -Pentane	2.3	9.6 ^h
Isoprene	0.055	0.23 ^b
<i>n</i> -Hexane	1.1	4.5 ^g
Benzene	4.4	19 ⁱ
Toluene	0.94	4.0 ⁱ

^aUnit of lifetimes is days. [OH] = 2.1×10^6 molecules cm⁻³ for July–August 2004. [OH] = 5.0×10^5 molecules cm⁻³ for January–February 2004.

^bAtkinson *et al.* [2005].

^cSchiffman *et al.* [1991].

^dAtkinson [1990].

^eVakhtin *et al.* [2003].

^fAtkinson [1986].

^gAtkinson [2003].

^hSekusak *et al.* [1999].

ⁱAnderson *et al.* [2003].

typical source profile is not very simple and is discussed in the next section.

[11] The compounds which showed distinct seasonal variations are ethane, ethyne, propane, and benzene (rsd = 49–55%). The winter maximum can be explained by the weaker OH sink which allows these compounds with relatively long tropospheric lifetimes (Table 4) to accumulate in the atmosphere and the maximum height of the boundary layer is at a seasonal low. The C₂–C₃ alkenes and toluene showed a similar pattern but their winter/summer ratios were lower because these gases cannot accumulate as much as the longer-lived compounds because of their shorter lifetime. The seasonal variation of C₄–C₆ alkanes was quite small (rsd = 10–22%), with the pentanes even showing an inverse pattern while the butanes still showed higher mixing ratios in winter. Considering that the major sink of C₄–C₆ alkanes is also OH oxidation and that their lifetimes are intermediate between C₂–C₃ alkenes and C₂–C₃ alkanes, this difference can be attributed to a change of source strength. As C₄–C₅ alkanes are known to be the main constituents in gasoline vapor [Kashimura *et al.*, 1983; Kirchstetter *et al.*, 1999; Petroleum Energy Center, 2004], it is assumed that the elevated evaporative emission counteracted the stronger sink in summertime and resulted in a small seasonal variation for those compounds. The inverse seasonal pattern of the pentanes indicates a significant contribution of evaporative emissions in summertime. The small seasonal variation of *n*-hexane also indicates the increase of evaporative emissions from its solvent use in summertime. The seasonal change of source contributions will be examined in more detail later.

[12] Isoprene showed no correlation with other observed NMHCs in the summer ($r^2 < 0.12$ in 2003 and $r^2 < 0.01$ in 2004). This indicates that isoprene was emitted predominantly from vegetation sources [Guenther *et al.*, 1993] whereas other measured NMHCs were emitted from anthropogenic sources. This is consistent with the fairly good correlation of summertime isoprene with solar radiation (UV-A and UV-B) and temperature ($r^2 = 0.76$ and 0.55 respectively without UV-A measurement in 2003 and $r^2 = 0.80$, 0.81 , and 0.68 , respectively in 2004). The time series of isoprene is plotted with simultaneously measured UV-A at Komaba in winter_2004 and summer_2004 in Figure 2. During both summer_2003 and summer_2004, the observed mixing ratios of isoprene followed the diurnal variation of UV-A intensity with little lag, which had a maximum at around noon. The rapid response of the ambient isoprene concentration to solar radiation indicates the rapid biosynthesis of this compound. The lifetime of isoprene in the troposphere is estimated to be only a few hours, which means that the level of this reactive compound during summer was mostly controlled by photosynthesis of the vegetation near the observation site. In winter, isoprene and UV-A, UV-B, and temperature showed no correlation ($r^2 = -0.06$, -0.05 , and 0.02 , respectively) and the atmospheric level of isoprene (0.02 ± 0.08 ppbv) was far less than the summertime value (0.23 ± 0.37 ppbv in 2003 and 0.28 ± 0.35 ppbv in 2004). Nighttime isoprene peaks in wintertime were occasionally observed in good correlation with other measured NMHCs when surface inversions were persistent (i.e., 28 January; Figure 2a), indicating the emission of isoprene from anthropogenic sources, most likely the combustion of gasoline [McLaren *et al.*, 1996; Reimann *et al.*, 2000]. On the contrary, the contribution of anthropogenic sources was negligible compared to the vegetation source in summer.

3.1.3. Influences of Meteorological Conditions

[13] Diurnal, day-to-day, and seasonal variations of meteorological conditions also play a fundamental role in controlling the NMHC concentrations. The majority of the measured species showed clear diurnal variations, with a nighttime maximum and a daytime minimum. This variation can be explained by weaker wind speed and the lower mixing depth, in addition to inactive photochemistry at night. For example, the average wind speed during summer_2004 was the lowest in early morning (1.5 ± 0.8 m s⁻¹ from 0400 to 0800 LT) and peaked in the afternoon (3.2 ± 0.8 m s⁻¹ around 1500 LT). Figure 3 shows the time series of wind speed, wind direction, and the volume mixing ratio of ethane, ethene, and toluene observed during summer_2004. The variations of ethane were similar to those of benzene and the measured C₃–C₆ alkanes, while the variations of ethene typified those of other measured C₂–C₄ alkenes. General patterns of toluene variation were similar to those of the alkanes, except that it occasionally showed sharp daytime peaks in addition to the normal diurnal peaks. Among the measured compounds, isoprene showed unique features, which were previously discussed in section 3.1.2.

[14] The mesoscale weather conditions also affect diurnal and day-to-day variations of NMHCs. When a high-pressure system was persistent, mixing ratio enhancements were observed both in early morning and at midday as seen on

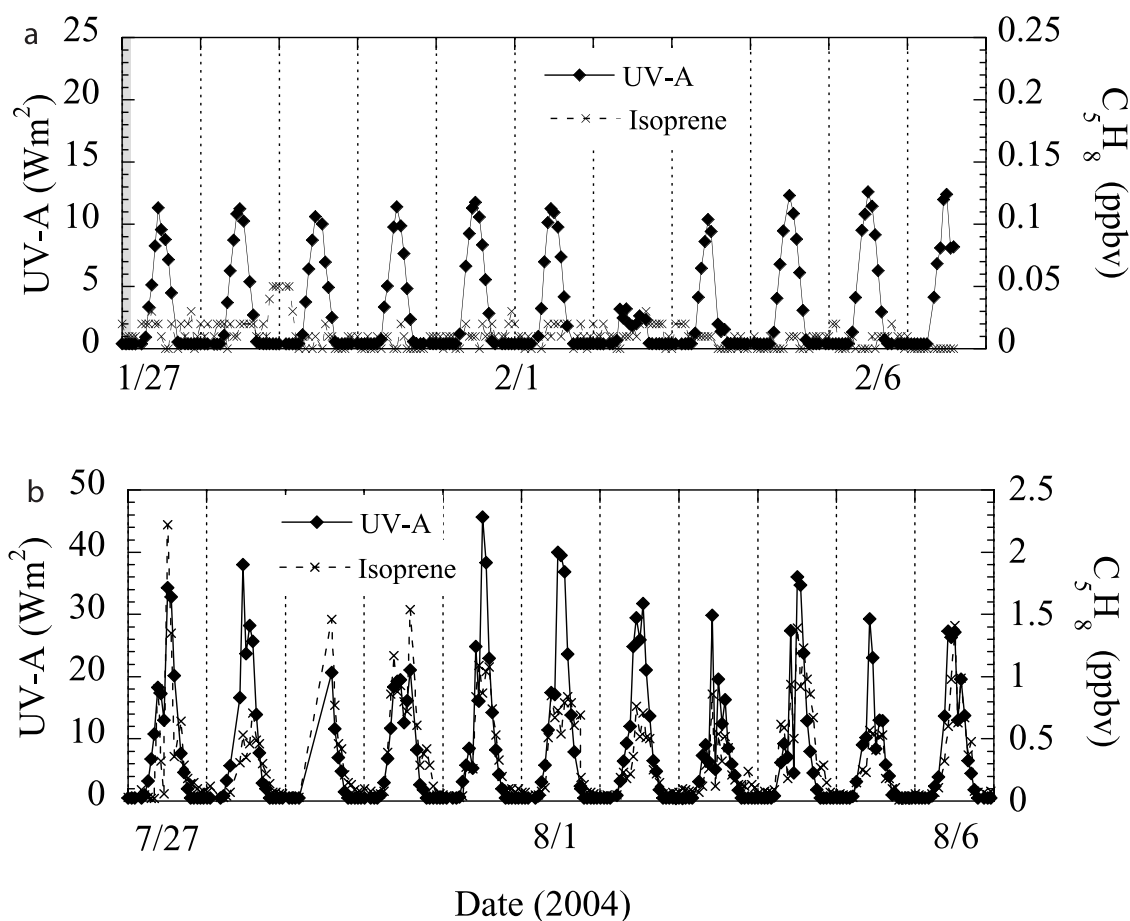


Figure 2. Time series of isoprene with simultaneously measured UV-A at Komaba in (a) winter_2004 and (b) summer_2004.

27 July and 11–14 August (Figure 3). Under these conditions, a southerly wind due to the sea breeze circulation system generally dominates during the daytime and it brings pollutants emitted around the coastal area of Tokyo Bay to the Komaba site and further inland (Figure 4) [Uno *et al.*, 1984; Wakamatsu *et al.*, 1983]. The mixing ratio enhancements in the early morning can be attributed to the accumulation of the trace gases in the nocturnal inversion formed by the radiation of heat from the ground at night [Wang *et al.*, 2001]. The afternoon peaks are interpreted to be the passage of the residual of the previous day's emission transported by the daytime sea breeze from the marine boundary layer in Tokyo Bay, where it has been stalled during the night, entraining fresh on-site emissions en route. In contrast, the mixing ratios of NMHCs stayed low when the wind speed increased because of typhoons passing through Tokyo (i.e., 29 July to 2 August and 5–6 August 2004, shown in Figure 3). To investigate the influences of wind speed and direction systematically, statistical analyses were performed. The mixing ratios were negatively correlated with wind speed for all of the observed NMHCs in all seasons ($-0.59 < -r^2 < -0.14$) except for isoprene ($-0.05 < -r^2 < 0.25$) of which the variation was strongly affected by solar radiation. The dominant wind direction varied with the season, from southerly in the summer (55% and 59% of the whole data set in 2003_summer and 2004_summer respectively) to northerly in autumn and winter (62% and

51% of the whole data set in 2003_autumn and 2004_winter) when the southerly and the northerly conditions were defined as $180 \pm 22.5^\circ$ and $0 \pm 22.5^\circ$, respectively. This seasonal change of dominant wind direction can be explained by the typical seasonal pressure pattern over Japan which is largely influenced by the Pacific high to the south in the summer and by the Siberian high to the north in the winter. It is necessary to consider this large wind bias carefully when determining the relationship between the mixing ratios and wind direction with these data sets.

[15] Further analyses on the influences of wind direction were done on the summer_2004 data. Figure 5 shows the relationship between the wind speed and the wind direction observed at the Komaba site during the summer_2004 campaign. The dominance of southerly conditions (SE + S + SW make up 75% of the total sample number) and the low wind speed of NW wind are quite noticeable. The NW wind was observed mainly at night when air is stagnant. Under such conditions, atmospheric compounds which have a relatively long lifetime accumulate in the air and show high mixing ratios. The relationship between the wind direction and CO mixing ratios is shown in Figure 6a. The atmospheric lifetime of CO in summer_2004 was estimated to be 23 days [Kanaya *et al.*, 2007], which could make this compound accumulate under stagnant condition, resulting in the significantly high level in the NW direction.

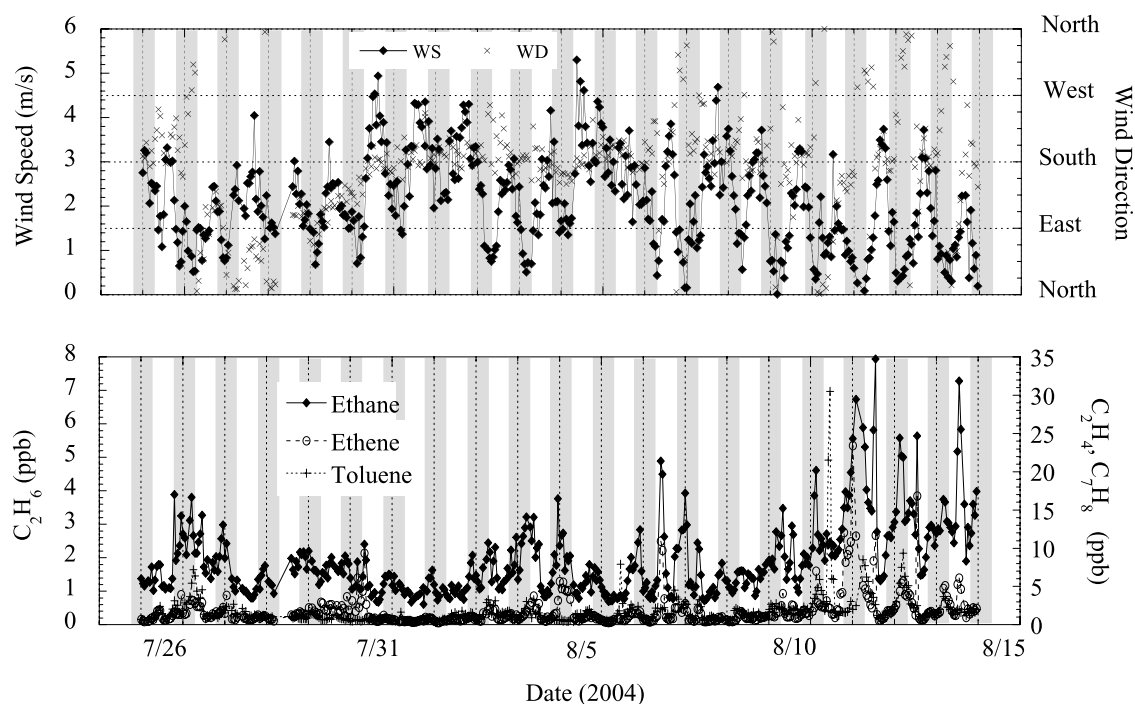


Figure 3. Time series of wind speed (m/s), wind direction, and the volume mixing ratio of ethane, ethene, and toluene observed at Komaba during summer_2004. Each column (separated by vertical dashed lines) corresponds to one day, starting at midnight. On each day the time from 1900 to 0700 LT is shaded to contrast daytime and nighttime.

Figure 6b shows the influence of wind direction on the mixing ratios of selected NMHCs using the method described below. To remove strongly stagnant or dispersed conditions, data were excluded when wind speed was lower than 0.5 m/s or higher than 4.0 m/s. In order to further reduce the wind speed dependence on wind direction analyses, ratios of increment of NMHC and CO ($\Delta\text{NMHC}/\Delta\text{CO}$) are shown for individual directions in Figure 6b. The increment of CO (ΔCO) was defined as the difference between the background level (set to 100 pptv) and the median value for each wind direction (Figure 6a). The increment for each NMHC (ΔNMHC) was defined as the difference between the minimum value and the average value during the observation period. Average values were used instead of median values for NMHCs because the signals from pollution events tend to fade when using median values. To better illustrate the feature of the 6 compounds in a single figure, the absolute values were factored in Figure 6b. Note that we used CO as a reference to evaluate the wind speed dependence of accumulation effects of pollutants. This is partly justified by the fact that emissions of CO are predominated by automobiles and they are considered to distribute rather uniformly in and around Tokyo so that wind direction dependence is small. The wind direction dependence of NMHCs is caused by the spatial distribution of sources; however, it also depends on the atmospheric lifetimes. Except propane and toluene, most of the observed NMHCs showed higher levels in the SE-S direction. Ethane and propene in Figure 6b represent the general features of long-lived compounds ($\tau \geq 4$ days) and short-lived compounds ($\tau < 3$ days), respectively. This indicated the influence from the emissions from central

Tokyo and coastal industrial areas located to the SE-S of the observation site (Figure 1). As described earlier, the isoprene level depends strongly on sunlight, showing that the N–W wind was common in nighttime and S–E wind was common in daytime. The larger bias of short-lived NMHCs (mostly alkenes) toward the SE–S direction indicates the relatively rapid transport of these compounds from industrial areas in the daytime. C_4 – C_5 alkanes, represented by i-pentane in Figure 6b, showed higher levels under the southerly conditions. Considering the large sample numbers for southerly conditions, nearly constant emission is expected in the south of Komaba. The higher density of cars and gas stations along the national road and the elevated expressway running approximately 1.5 km south of the observation site could be a contributing source. Among the observed NMHCs, propane showed the least dependency on wind direction. This can be explained by common propane use in residential areas in the suburbs. Toluene showed the pollution rose in the east direction as shown in the sharp increase in the daytime on 11 August (Figure 3). Aside from this extreme event, toluene showed elevated levels in N–E winds compared to other wind sectors. The source distribution for each compound will be discussed in more detail in the following sections.

3.2. Seasonal Changes in Source Contributions in Central Tokyo

3.2.1. Prior Studies on the Major Source Types in Urban Areas in Japan

[16] There has been considerable effort to construct a reliable emission inventory of atmospheric pollutants both by bottom-up and top-down approaches. Bottom-up inven-

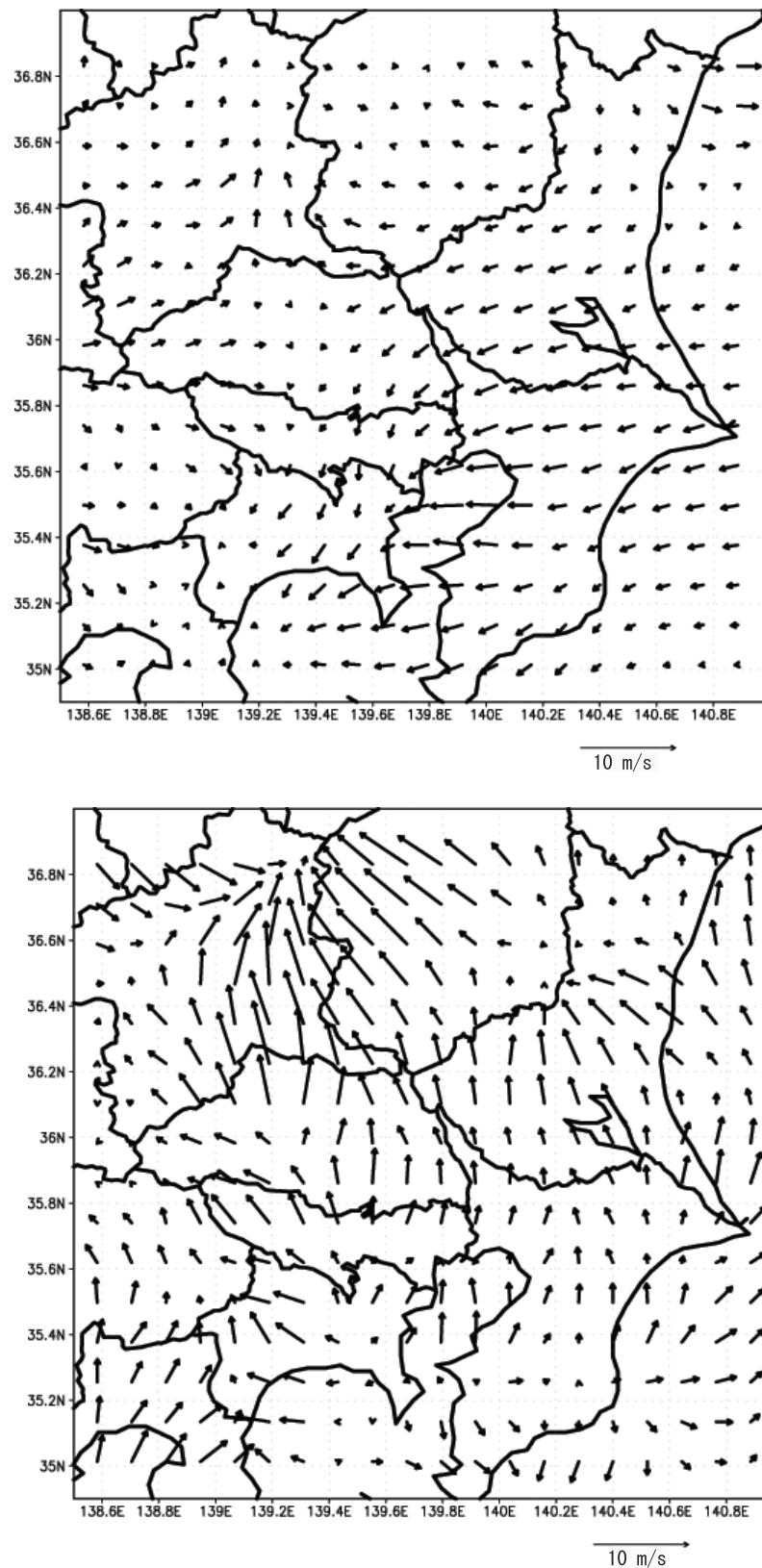


Figure 4. Surface wind vectors over the Kanto district on 12 August 2004 created by the MM5 meteorological model nudged by the RANAL (regional objective analysis) data of the Japan Meteorological Agency (JMA), AMeDAS (Automated Meteorological Data Acquisition System) data of JMA, and AEROS (Atmospheric Environmental Regional Observation System) of MOE at the local time (Japan standard time) of (a) 0200 LT and (b) 1400 LT.

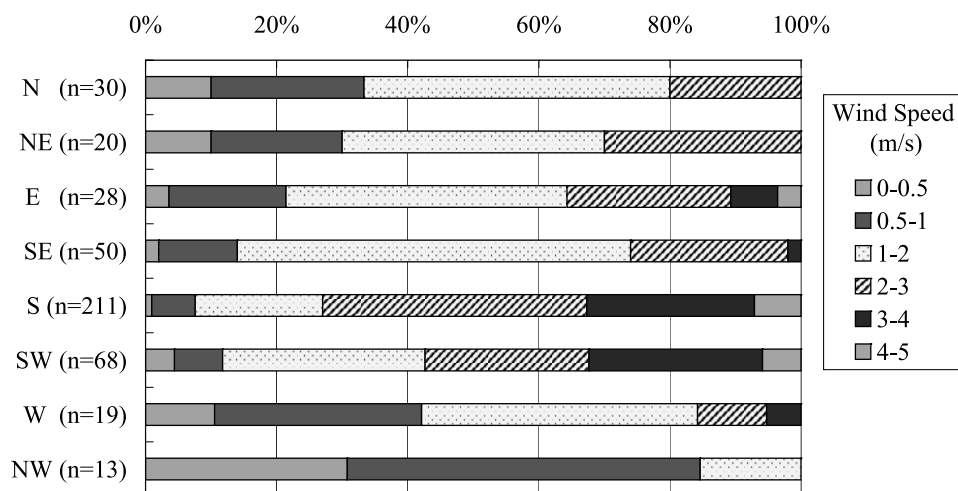


Figure 5. Fraction of observed wind speed for eight 45° wind direction sectors, with centers at 0°(N), 45°(NE), 90°(E), 135°(SE), 180°(S), 225°(SW), 270°(W), and 315°(NW). Both wind speed and wind direction were observed at the rooftop of the building at the Komaba site (approximately 18 m above the ground) during the summer_2004 campaign. The numbers *n* in parentheses denote the sample numbers for each wind sector and add up to the total sample number (439) for summer_2004.

tories are constructed on the basis of the statistics about fuel consumption, production, vehicle and other source activities, by applying the emission factors examined for each of the sources. The problem is that it is not easy to obtain detailed information in the central city where multiple sources are concentrated and have different temporal variations. The PRTR reports are very useful for this purpose but the compounds the law covers are still limited.

[17] The identification and quantification of sources of atmospheric pollutants have also been conventionally attempted using receptor-oriented models [Miller *et al.*, 2002]. There are a few previous studies that applied the chemical mass balance (CMB) receptor model [Watson *et al.*, 2001, and references therein] to urban atmospheric NMHCs in Japan [Tanaka *et al.*, 1993; Wadden *et al.*, 1986]. The CMB model is a powerful tool when all major sources are identified with their chemical compositions well characterized and the emission profiles do not change between the source and the receptor. However, this is not the case in urban studies because of the lack of integrated data on emission profiles of vehicle exhaust, which vary a lot depending on the vehicle types, the driving modes, the ambient temperature, etc. Considering the uncertainty of the source profiles, correlations among the measured species were used to identify the sources of atmospheric pollutants in this study.

[18] For reference to possible sources in urban area, the source profiles used in the studies by Tanaka *et al.* [1993] are shown in Table 5, with the detailed vehicle source profile taken from Tanaka *et al.* [2001a]. We must note that Table 5 only considers 12 compounds measured in this study. We can briefly divide the sources in Table 5 into “vehicle exhaust” and “evaporative emissions” because the sources other than vehicle exhaust (solvent, gasoline vapor, petroleum refinery, and chemical plants) are all caused by some kind of evaporative processes, thus the emission is likely correlated with temperature.

[19] Gasoline vapor is dominated by C₄–C₅ alkanes as already described and ethene accounts for more than 50% of

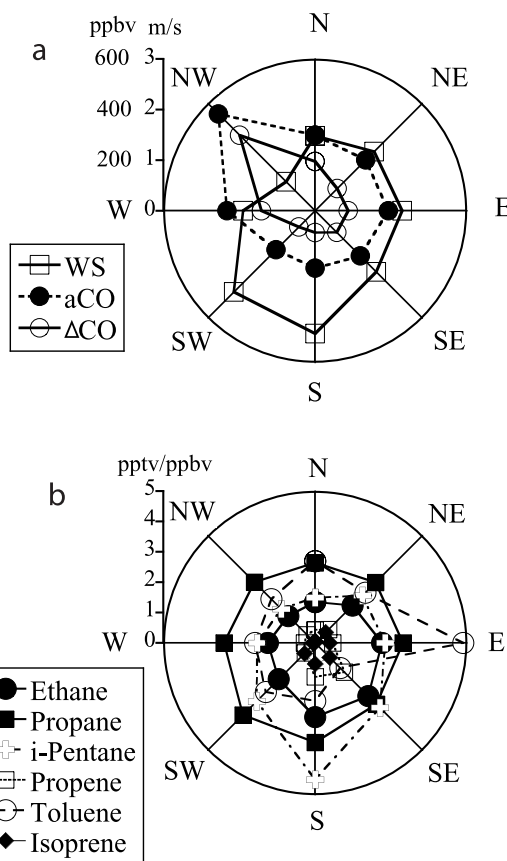


Figure 6. Influence of wind direction on parameters observed during the summer_2004 campaign. Wind sectors are defined as in the caption for Figure 5. Data were excluded when wind speed was lower than 0.5 m/s or higher than 4.0 m/s. (a) Wind speed and averaged mixing ratios (aCO) and normalized increment of median mixing ratios (ΔCO) of carbon monoxide. (b) Averaged mixing ratios of ethane, propane, i-pentane, propene, toluene and isoprene normalized by ΔCO. See text for detailed descriptions.

Table 5. Chemical Composition of Major NMHCs Sources in Japan Normalized to the Measured 12 Component Hydrocarbons^a

	Vehicle Profile ^b					Paint Solvent ^c	Gasoline Vapor ^c	Petroleum Refinery ^c	Chemical Plant ^c
	LDG	SLD	LPG	LDD	HDD				
C ₂ H ₆	5.59	3.41	8.86	4.56	1.79	0.00	0.00	3.30	3.22
C ₂ H ₄	21.75	24.95	1.76	29.25	57.41	0.00	0.00	3.19	53.59
C ₂ H ₂	4.19	12.69	0.00	19.13	11.53	0.00	0.00	1.76	1.93
C ₃ H ₈	0.34	0.29	24.84	0.00	0.00	0.00	2.00	22.20	4.61
C ₃ H ₆	8.31	15.21	0.00	18.25	13.56	0.00	0.00	3.08	4.18
<i>i</i> -C ₄ H ₁₀	2.09	1.60	21.16	4.30	1.07	0.00	16.87	7.36	2.79
<i>n</i> -C ₄ H ₁₀	4.19	3.15	43.38	3.36	2.27	0.00	21.20	17.69	5.89
<i>i</i> -C ₅ H ₁₂	4.79	9.77	0.00	4.56	0.33	0.00	39.73	15.82	4.29
<i>n</i> -C ₅ H ₁₂	10.91	5.95	0.00	3.72	1.97	0.00	14.54	7.58	3.00
<i>n</i> -C ₆ H ₁₄	4.50	1.16	0.00	0.73	1.97	13.72	3.55	5.49	4.61
C ₆ H ₆	12.75	8.14	0.00	8.13	5.13	0.00	1.00	4.73	3.64
C ₇ H ₈	20.60	13.67	0.00	4.02	2.97	86.28	1.11	7.80	8.25
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

^aUnit is weight percent (wt %).^bLDG, light-duty gasoline; SLD, super-light-duty gasoline; LPG, liquid petroleum gas-fueled; LDD, light-duty diesel; HDD, heavy-duty diesel.^cTanaka *et al.* [1993, 2001a].

chemical plant emissions. Ethene and propene are widely used as industrial materials in Japan. The domestic production and consumption in 2005 were 7.6 Gg and 3.0 Gg for ethane, and 6.0 Gg and 2.4 Gg for propene respectively [Ministry of Economy, Trade and Industry, 2006]. The composition of vehicle emissions varies greatly depending on vehicle type and driving modes. It also changes over time reflecting the enforcement of the national regulations on automobiles and fuel which have been constantly tightened in stages. The ratios shown in Table 5 are only a reference, but we can still see some distinct features. For example, the main components of LPG car emissions are propane and butane and those from diesel cars are ethene, propene, and ethyne whereas gasoline cars emit all 12 compounds with some emphasis on ethene and aromatics (toluene and benzene). According to the Statistical Survey on Motor Vehicle Transport for FY2004 [MLIT, 2005], gasoline accounted for 63% of the total annual fuel consumption by cars, followed by diesel oil (34%) and LPG (3%). Considering the good gas mileage of diesel cars, emissions from gasoline cars should be dominant in the vehicle emissions category shown in Table 5.

3.2.2. Emission Estimates Based on the Correlations of NMHCs With CO and Ethyne

[20] When a certain data set shows a good correlation among compounds which share common sources, the slopes of the regression lines can be used as emission ratios. When deriving emission ratios for NMHCs, CO and ethyne are often used as the reference compounds, as they are known to be good tracers of combustion and especially of car exhaust in urban areas [Bonsang and Boissard, 1999]. Tables 6a and 6b show the correlation coefficients for each pair of observed NMHCs at Komaba in the winter and summer of 2004. During summer_2004 isoprene showed a very tight correlation with solar flux and the temperature (section 3.1), but no correlation with other observed NMHCs (Table 6b). Other NMHCs correlated fairly well with each other but the correlations were generally much stronger in winter than in summer. During winter most of these NMHCs also correlated well with CO, indicating a combustion-type source, most likely tailpipe emissions from automobiles. The correlation with CO was poor for C₄–C₅

alkanes, alkenes, and toluene in the summer. This indicates the increased contribution of evaporative NMHC sources in summer [Kourtidis *et al.*, 1999].

[21] Since the winter_2004 data set showed the dominance of a single combustion-type source, the typical emission ratios for wintertime were derived for observed NMHCs on the basis of both CO and ethyne, respectively (Table 7). The emission ratios were derived from the slopes of regression lines of one of the NMHCs and CO or ethyne, assuming that the effect of aging, mixing, and dilution of air masses during the transport is negligible for CO and ethyne. This assumption is acceptable with the estimated lifetime of ethyne (= 30 days as shown in Table 4) and CO (= 96 days when calculated under the same condition as in Table 4). Although the correlation coefficients were not very high for several compounds such as *n*-hexane and toluene, because some data were affected by sources other than car exhaust (i.e., temporal solvent use), their emission ratios (the slopes of regression lines) were not affected greatly by these minor scatterings. For some alkenes and *n*-hexane, a few obvious outliers have been omitted from the total of 342 data points to better obtain the slope from the single dominant source (= car exhaust). These values can be considered as emission ratios for the compounds, of which the lifetimes are longer than the typical transport time (presumably half a day), but not for short-lived compounds such as the butenes. For those reactive compounds, the values presented in Table 7 should be regarded as the typical ratios in central Tokyo (near Komaba) during wintertime, as the integration of all effects from mixing, dilution, and transport. C₂–C₃ alkanes showed higher correlation with CO than with ethyne indicating the considerable contribution from combustion-type sources other than automobile exhaust (i.e., heating fuel).

[22] For the summer data set, the correlation plots were much more scattered because of the effects of multiple sources and faster decomposition rates. Therefore it was not possible to break those data into groups and derive emission ratios for different sources. It was not useful to trace back the plume's origins using the wind data because the plumes were the integration of different, colocated sources. As already described above, the mixing ratio of the NMHCs had little correlation with wind direction but correlated well

Table 6a. Correlation Coefficients Among Observed NMHCs and CO at Komaba in Winter_2004

	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>trans</i> -2-C ₄ H ₈	1-C ₄ H ₈	<i>cis</i> -2-C ₄ H ₈	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	C ₅ H ₈	<i>n</i> -C ₆ H ₁₄	C ₆ H ₆	C ₇ H ₈
Ethene	0.85															
Ethyne	0.84	0.95														
Propane	0.94	0.86	0.84													
Propene	0.64	0.87	0.89	0.65												
<i>i</i> -Butane	0.82	0.93	0.97	0.83	0.93											
<i>n</i> -Butane	0.89	0.94	0.97	0.89	0.88	0.99										
<i>trans</i> -2-Butene ^a	0.58	0.80	0.87	0.58	0.97	0.93	0.86									
1-Butene	0.59	0.81	0.87	0.59	0.97	0.93	0.86	1.00								
<i>cis</i> -2-Butene	0.58	0.80	0.86	0.58	0.97	0.93	0.86	1.00	1.00							
<i>i</i> -Pentane	0.74	0.90	0.95	0.74	0.96	0.99	0.95	0.97	0.97	0.97						
<i>n</i> -Pentane	0.66	0.85	0.91	0.65	0.98	0.96	0.91	0.99	0.99	0.99	0.99					
Isoprene	0.56	0.79	0.86	0.56	0.97	0.92	0.85	1.00	1.00	1.00	0.96	0.99				
<i>n</i> -Hexane	0.63	0.84	0.90	0.62	0.98	0.95	0.89	0.99	1.00	0.99	0.98	1.00	0.99			
Benzene	0.66	0.86	0.91	0.65	0.98	0.96	0.91	0.99	0.99	0.99	0.99	1.00	0.99	1.00		
Toluene	0.77	0.88	0.92	0.81	0.82	0.90	0.91	0.79	0.79	0.78	0.88	0.83	0.77	0.82	0.83	
CO	0.88	0.81	0.87	0.88	0.38	0.90	0.91	0.87	0.78	0.85	0.86	0.83	-0.27	0.60	0.83	0.70

^aThere was no measurement for 1,3-butadiene during winter_2004.

with wind speed. However, the correlations among NMHCs were generally good when the data comprising the plume events were extracted, which means that the relative fraction of each compound in each peak was conserved while the plumes were passing the observation site. Thus for the summer data set, the plume characteristics were investigated solely using chemical composition by using the relative fraction of NMHCs to give information about the sources and the freshness of the plumes.

3.2.3. Chemical Composition of Peaks Observed in Summer

[23] From the summer_2004 data set, the chemical composition was derived for eight selected peaks (Figure 7). Peaks 1–8 were observed on 26–27 and 31 July, and on 4–5, 7, 10–11, 11–12, 12–13, and 13–14 August, respectively. Some peaks were observed at night and others were observed during the daytime. Among the twelve listed compounds, toluene showed the largest variation. For example, toluene showed a sharp increase in plume 5 (Figure 7), which may reflect local solvent use. The relative fraction of the compounds also reflects the air mass age of each plume. On the basis of the relatively high fraction of

alkenes, which are short-lived, plumes 2, 3, and 6 were considered to be less photochemically processed than the other plumes. The large variation of the alkene fraction, as compared to other relatively more stable compounds in the 8 plumes, suggests that the typical transport time from the source regions to the observation site is within a few days.

[24] As explained below, the 8 summertime peaks were classified into 4 different plume categories: (1) nighttime accumulation affected by urban/industrial sources (plumes 1 and 7); (2) nighttime accumulation affected by petrochemical industries (plumes 2, 3, and 6); (3) daytime plumes affected by fuel evaporation (plumes 4 and 8); and (4) daytime plumes affected by local toluene emissions (plume 5) (Table 8). The ratio of the average NMHC composition for each plume category extracted from the summer_2004 data set relative to that from the winter_2004 data set (Table 7) and normalized to ethyne is shown in Table 8. The closer the summer composition is to the winter value, the closer the ratio becomes to 1. In Table 8 most of the compounds show a ratio greater than 1, indicating an additional contribution of sources other than car exhaust. The categorization was based on the characteristic chemical

Table 6b. Same as Table 6a but for Summer_2004

	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	1-C ₄ H ₈	<i>cis</i> -2-C ₄ H ₈	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	1,3-C ₄ H ₆	C ₅ H ₈	<i>n</i> -C ₆ H ₁₄	C ₆ H ₆	C ₇ H ₈
Ethene	0.74															
Ethyne	0.80	0.50														
Propane	0.84	0.54	0.74													
Propene	0.59	0.87	0.32	0.42												
<i>i</i> -Butane	0.86	0.55	0.77	0.78	0.39											
<i>n</i> -Butane	0.75	0.46	0.66	0.66	0.33	0.94										
1-Butene	0.51	0.75	0.25	0.39	0.78	0.39	0.34									
<i>cis</i> -2-Butene	0.20	0.27	0.04	0.18	0.40	0.20	0.22	0.56								
<i>i</i> -Pentane	0.69	0.44	0.56	0.59	0.30	0.90	0.95	0.33	0.22							
<i>n</i> -Pentane	0.55	0.36	0.42	0.45	0.25	0.77	0.92	0.29	0.24	0.94						
1,3-Butadiene ^a	0.31	0.51	0.16	0.28	0.57	0.22	0.18	0.67	0.42	0.16	0.16					
Isoprene	-0.21	-0.13	-0.16	-0.20	-0.15	-0.09	-0.07	-0.15	-0.08	0.00	0.01	-0.14				
<i>n</i> -Hexane	0.73	0.74	0.51	0.58	0.65	0.70	0.65	0.65	0.36	0.64	0.58	0.47	-0.11			
Benzene	0.71	0.59	0.53	0.57	0.44	0.72	0.63	0.41	0.21	0.68	0.53	0.26	0.00	0.63		
Toluene	0.37	0.21	0.54	0.42	0.12	0.40	0.32	0.12	0.05	0.24	0.17	0.11	-0.12	0.24	0.25	
CO	0.85	0.54	0.88	0.79	0.36	0.84	0.70	0.31	0.05	0.64	0.45	0.19	0.56	-0.14	0.73	0.48

^aThere was no measurement for *trans*-2-butene during summer_2004.

Table 7. Emission Ratios (ER) of Light Hydrocarbons Relative to Ethyne and Carbon Monoxide Observed in Central Tokyo in January 2004

	C ₂ H ₂ , ppt/ppt		CO, ppt/ppm	
	ER	r ²	ER	r ²
C ₂ H ₆	2.2	0.69	12.4	0.83
C ₂ H ₄	1.5	0.71	7.4	0.70
C ₂ H ₂	1.0	1.00	4.6	0.81
C ₃ H ₈	2.9	0.67	16.5	0.84
C ₃ H ₆	0.4	0.69	2.3	0.69
<i>i</i> -C ₄ H ₁₀	0.9	0.78	5.0	0.89
<i>n</i> -C ₄ H ₁₀	1.3	0.78	7.1	0.89
<i>trans</i> -2-C ₄ H ₈	0.1	0.83	0.6	0.86
1-C ₄ H ₈	0.1	0.66	0.6	0.66
<i>i</i> -C ₄ H ₈	0.1	0.82	0.5	0.83
<i>cis</i> -2-C ₄ H ₈	0.1	0.82	0.4	0.81
<i>i</i> -C ₅ H ₁₂	0.7	0.81	3.6	0.88
<i>n</i> -C ₅ H ₁₂	0.3	0.81	1.5	0.85
<i>n</i> -C ₆ H ₁₄	0.2	0.63	1.0	0.53
C ₆ H ₆	0.2	0.81	1.0	0.80
C ₇ H ₈	1.5	0.62	6.6	0.55

composition of each category. The compounds specifically enhanced in the category 2 plumes were C₂–C₄ alkenes and *n*-hexane and benzene. The olefins are often used as chemical intermediates and polymer components in petrochemical manufacturing. The enhancement of industrial solvents (*n*-hexane and benzene) also indicates the input from the chemical industry. The peaks of category 2 were observed at nighttime after daytime southerly winds were persistent. This indicates that these reactive compounds were transported from the coastal industrial area located south of the Komaba observation site and accumulated during the night when the air is stagnant and photochemistry is inactive. Category 3 was characterized by C₄–C₅ alkane levels that were up to 2–5 times higher than the

winter ratio. The buildup of butanes and pentanes are the result of daytime fuel evaporation. The Japan Clean Air Program (JCAP) has estimated the relative contribution of different types of hydrocarbon emissions from automobiles. In addition to the normal tailpipe emissions from running cars, it is known that cars also emit significant amounts of hydrocarbons (1) just after starting, when the engine is still cold (cold start emission); (2) from the fuel tanks of parked cars (DBL: diurnal breathing loss); and (3) from the intake pipe within an hour from the engine being stopped (HSL: hot soak loss). On a hot day in August, the fraction of hydrocarbon emissions from stabilized tailpipe emissions, cold start emissions, DBL, and HSL was reported to be 66, 19, 14, and 1%, respectively [Petroleum Energy Center, 1999]. The amount of DBL largely depends on ambient temperature, and thus the above value should be considered as the maximum value for the DBL fraction. Although the DBL contribution to total hydrocarbon emissions is still smaller than the tailpipe fraction, 14% is still significant for the C₄–C₅ alkanes, which are the main constituents of the evaporative emissions of gasoline. Gasoline evaporation from gas stations is also expected to significantly contribute to the daytime increase of C₄–C₅ alkanes. In category 4, the enhancement of toluene was 4 times larger than the winter value. The episodic increases of its daytime levels suggest a considerable source distribution in the vicinity of the observation site. Toluene is also emitted from automobiles, though to a much lesser extent than from solvent use. In Japan the ratio of toluene emission from solvent use relative to automobiles was estimated to be 85%:15% in 2002 [Ministry of Environment of Japan (MOE), 2004]. Therefore solvent usage is the most likely toluene source, and the enhanced levels in summer versus winter may be explained by temperature-driven evaporation.

[25] Because UCI canister samples were occasionally collected at the Komaba site, an extended set of hydrocar-

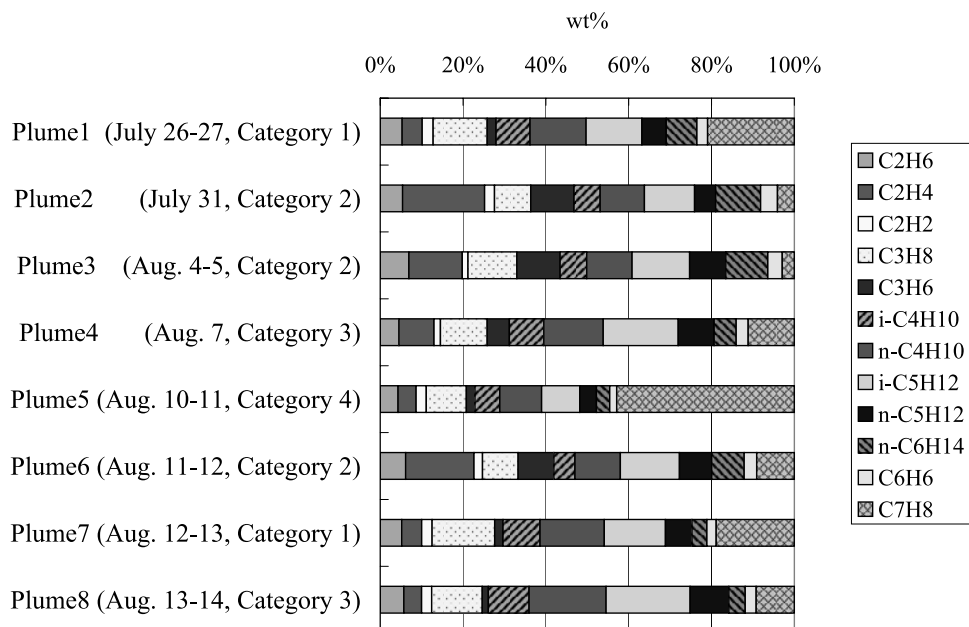
**Figure 7.** Relative fraction of light hydrocarbons in plumes identified from the summer_2004 data set (wt %).

Table 8. Ratios of NMHC Composition for the Plume Categories Extracted From the Summer_2004 Data Set Relative to the NMHC Composition From the Winter_2004 Data Set, Normalized by Ethyne

	Category 1	Category 2	Category 3	Category 4
C ₂ H ₆	0.79	1.22	0.99	0.68
C ₂ H ₄	1.18	5.27	2.01	1.12
C ₂ H ₂	1.00	1.00	1.00	1.00
C ₃ H ₈	1.11	1.01	1.20	0.80
C ₃ H ₆	1.13	7.00	2.37	1.18
<i>i</i> -C ₄ H ₁₀	1.60	1.47	2.20	1.18
<i>n</i> -C ₄ H ₁₀	1.93	1.90	2.83	1.41
<i>i</i> -C ₅ H ₁₂	2.82	3.53	4.96	1.93
<i>n</i> -C ₅ H ₁₂	2.82	4.35	5.34	1.94
<i>n</i> -C ₆ H ₁₄	3.02	6.96	3.30	1.85
C ₆ H ₆	1.31	2.51	1.94	0.95
C ₇ H ₈	1.74	0.62	1.15	3.95

bon and halocarbon concentrations for plumes 1 and 2 were available. Five samples collected while plume 1 was passing over the Komaba site showed remarkable enhancements of halocarbons indicative of industrial emissions (i.e., CHCl₃, C₂HCl₃, C₂Cl₄, Halon-2402, and HCFC-142b, were 5–13 times higher than the median concentrations measured at the Komaba site in 2004 summer). By contrast, the enhancement of these halocarbons was not significant (–66% to +94% of the median 2004_summer concentrations at Komaba) in a sample collected when plume 2 was passing the Komaba site. The high levels of the above halocarbons and toluene are consistent with the influence of industrial

emissions for category 1, and the moderate levels of the above halocarbons and high levels of alkenes and benzene are consistent with input from petrochemical industries and automotive emissions for category 2.

[26] These observations indicate that the summer enhancement of evaporative emissions in Tokyo is contributing to the increased fraction of C₄–C₅ alkanes, C₂–C₃ alkenes, hexane, benzene and toluene being up to 7 times greater than the wintertime fractions (Table 8), assuming ethyne is constantly emitted from automobiles all year round.

3.3. Comparison With Observations in a Suburban Area

[27] In this study, a comparison was made between central Tokyo and a suburban area using the IMPACT observations at Komaba and Kisai in summer_2004 (section 2). The observed concentrations measured at the Kisai site are shown in Table 9. When compared to Table 1, the median concentrations of almost all of the measured NMHCs were not significantly different for central Tokyo (Komaba) and the suburban area (Kisai). Rather, the levels of some compounds were higher in the suburban area than in the central city. In particular, average toluene levels were higher by a factor of 2 at Kisai compared to Komaba. Figure 8 shows the time series of ethane, ethene, and toluene in Kisai on the same scale as in Figure 3. Sea breeze circulation systems were dominant on sunny days when the atmospheric pressure gradients were small, such as 26–28 July and 6 and 10–14 August (Figure 4). In such

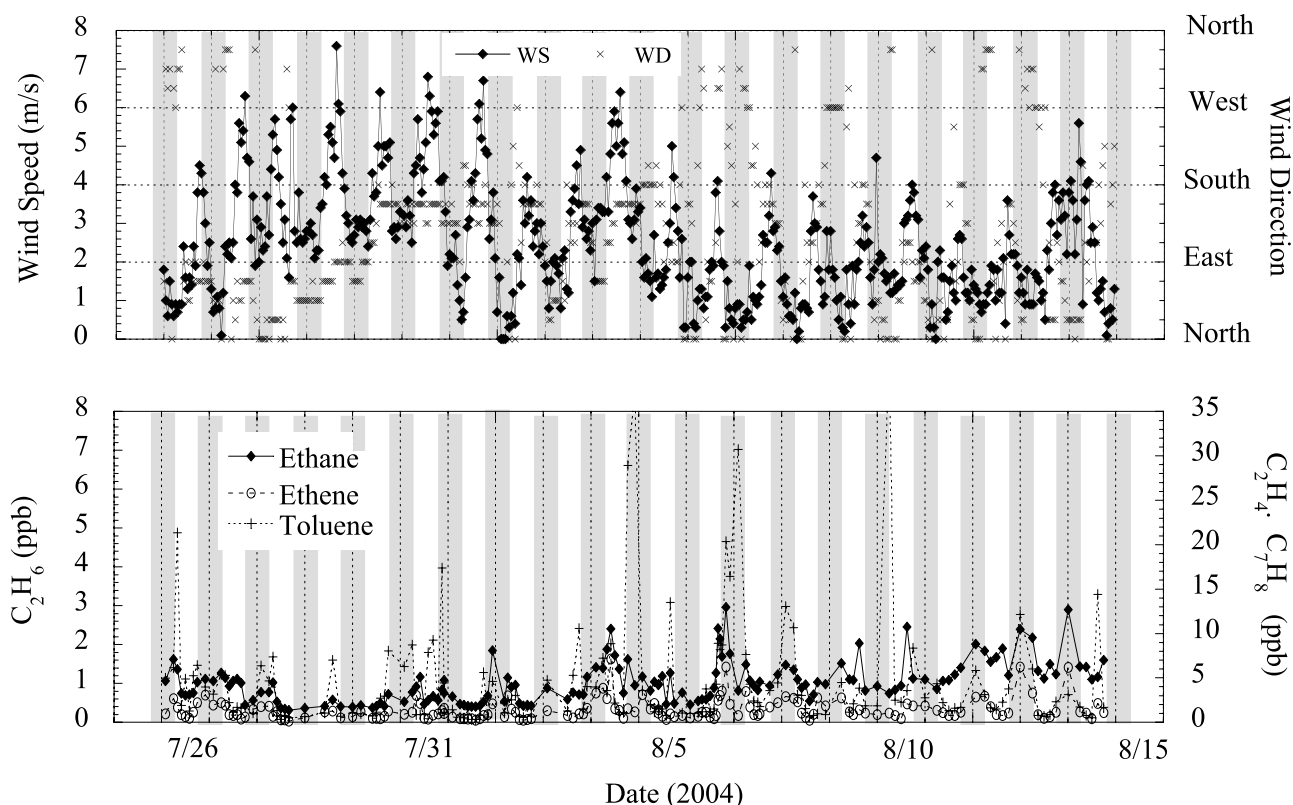


Figure 8. Time series of wind speed and the volume mixing ratio of ethane, ethene, and toluene observed at Kisai during summer_2004. (Columns and shading conform to those of Figure 3.)

Table 9. Median Mixing Ratios With the 25th and 75th Percentiles and the Minimum and the Maximum of 16 NMHCs Measured at the Kisai Site in Summer_2004^a

Compounds	Median	25–75%	Minimum–Maximum
Ethane	1.02	0.64–1.33	0.34–3.20
Propane	2.11	1.31–3.03	0.23–30.0
<i>i</i> -Butane	0.88	0.61–1.38	0.20–55.8
<i>n</i> -Butane	1.50	0.98–2.24	0.31–107
<i>i</i> -Pentane	1.09	0.70–1.71	0.05–141
<i>n</i> -Pentane	0.52	0.35–0.82	0.08–69.0
<i>n</i> -Hexane	0.28	0.17–0.48	0.05–13.2
Ethene	1.19	0.74–2.06	0.17–8.12
Propene	0.32	0.16–0.60	0.04–3.36
<i>cis</i> -2-Butene	0.07	0.03–0.12	0.01–15.4
1,3-Butadiene	0.04	0.02–0.07	0.01–0.75
Ethyne	0.82	0.54–1.22	0.16–8.60
Benzene	0.22	0.13–0.32	0.03–2.29
Toluene	2.18	1.08–4.84	0.31–39.7

^aUnit is ppbv.

cases, the effect of pollutant outflow from the Tokyo Bay area to its suburbs must be taken into account. During these periods, increased baseline levels of ethane, ethyne, and propane were observed, indicating the buildup lasted for several days in the semiclosed circulation, whereas other shorter-lived NMHCs showed less or no clear indication of enhancement. The diurnal variations of the measured NMHCs did not clearly reflect the contribution of transport from central Tokyo, although this could in part be due to the coarser sampling time resolution at Kisai.

[28] Among the NMHCs observed at Kisai, the C₂–C₄ alkenes, 1, 3-butadiene and benzene correlated fairly well with each other ($r^2 > 0.47$; Table 10). The common major source of these compounds in urban areas is tailpipe emissions from automobiles. Although benzene is emitted from both automobiles and solvent use, the domestic ratio of benzene emissions from car exhaust and solvent use was estimated to be 86%:14% in 2002 [MOE, 2004]. Large amounts of 1,3-butadiene are emitted from automobile exhaust as well (89% of total 1,3-butadiene emissions), followed by 8% from the chemical industry and 2% from cigarette smoke [MOE, 2004]. Given that these very short lived compounds correlated well, their major source near Kisai was considered to be tailpipe emissions from local traffic.

[29] Although the C₄–C₅ alkanes are also emitted from tailpipe emissions of automobiles, they are the main components of gasoline evaporation from fuel tanks of parked cars (DBL) and from the fueling process at gas stations. However, their emission from gas stations has been significantly reduced by installing so-called “vapor-return systems,” which recover the fuel vapor from the vent pipe using a filtering device. The system has been installed at more than 90% of gas stations in both Tokyo and Saitama in response to ordinances by each city which took effect in 2001 and 2002, respectively. Assuming that the system is contributing to reduce the evaporation at gas stations, the major sources of C₄–C₅ alkanes at Komaba and Kisai are assumed to be tailpipe emissions and DBL. The very high maximum for C₄–C₅ alkanes at Kisai indicates the occasional large emissions in the vicinity of the site.

[30] The correlations among the NMHCs measured at Kisai show that the enhancement of toluene was independent from the other NMHCs (Table 10), indicating its emission from solvent use. Even though *n*-hexane and benzene are also industrial solvents (section 3.2), the correlation between toluene and *n*-hexane and benzene ($r^2 < 0.47$) suggests that the industrial sources of toluene are not colocated with industrial *n*-hexane and benzene sources. The strong enhancement of toluene in Kisai is consistent with domestic statistics, which suggest an extremely large emission of toluene in Saitama Prefecture (where Kisai is located). In 2004, toluene emissions in Saitama Prefecture were 15 Mt, of which the major source was manufacturing. This was the second highest in the nation [MOE, 2005]. By comparison, toluene emissions in Tokyo were 1.5 Mt in 2004, as it has significantly decreased in response to emission controls in the printing industry [MOE, 2005]. The large difference between 75% and 25% percentile values of toluene at Kisai (Table 9) indicates the active emission of toluene in the area.

[31] Ambient levels of the C₂–C₃ alkanes often reflect local energy use although they are also emitted in car exhaust. In Japan, natural gas is commonly used in cities while liquefied petroleum gas (LPG) is widely used in the suburbs. For example, the typical gas used in Tokyo is composed of 70–90 wt % methane, <20 wt % ethane, <20 wt % propane, and <10 wt % butane (Tokyo Gas, Gas

Table 10. Correlation Coefficients of C₂–C₇ NMHCs and CO at Kisai in Summer_2004

	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	1-C ₄ H ₈	<i>cis</i> -2-C ₄ H ₈	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	1,3-C ₄ H ₆	C ₅ H ₈	<i>n</i> -C ₆ H ₁₄	C ₆ H ₆	C ₇ H ₈
Ethene	0.75															
Ethyne	0.64	0.68														
Propane	0.43	0.34	0.45													
Propene	0.61	0.91	0.54	0.31												
<i>i</i> -Butane	0.68	0.66	0.44	0.36	0.54											
<i>n</i> -Butane	0.69	0.66	0.44	0.37	0.56	0.98										
1-Butene	0.63	0.88	0.56	0.28	0.92	0.59	0.59									
<i>cis</i> -2-Butene	0.36	0.60	0.48	0.40	0.66	0.43	0.45	0.79								
<i>i</i> -Pentane	0.78	0.68	0.56	0.29	0.54	0.67	0.69	0.66	0.49							
<i>n</i> -Pentane	0.76	0.69	0.57	0.26	0.56	0.68	0.71	0.65	0.46	0.98						
1,3-Butadiene	0.48	0.82	0.55	0.25	0.79	0.55	0.54	0.81	0.71	0.48	0.49					
Isoprene	0.18	0.23	0.14	0.38	0.34	0.32	0.27	−0.05	−0.21	0.31	0.26	−0.33				
<i>n</i> -Hexane	0.43	0.49	0.37	0.17	0.44	0.46	0.49	0.46	0.40	0.46	0.49	0.41	0.20			
Benzene	0.86	0.85	0.76	0.32	0.71	0.67	0.66	0.73	0.47	0.76	0.78	0.65	0.28	0.47		
Toluene	0.26	0.28	0.23	0.20	0.33	0.18	0.20	0.36	0.34	0.27	0.26	0.27	0.02	0.46	0.24	
CO, ppbv	0.76	0.67	0.54	0.30	0.52	0.61	0.57	0.53	0.28	0.59	0.57	0.48	0.32	0.31	0.75	0.17

quality of the city gas 13A, <http://www.tokyo-gas.co.jp/msds/seijou.html>) while typical LPG for domestic use is composed of 98% propane, 1% ethane, and 1% butane (Japan LP Gas Association, unpublished data, 2002). Given that the propane peaks at Kisai were very sharp and independent of any of the measured NMHCs (Table 10), the roughly 20% higher propane levels observed at Kisai than at Komaba may be due to propane leakage from local LPG use. Similarly, the higher fraction of natural gas use in the cities may contribute to the 50% higher level of ethane observed at Komaba than at Kisai. Recently, the use of vehicles fueled with compressed natural gas (CNG) has been promoted in metropolitan Tokyo. The increasing numbers of CNG vehicles and CNG fueling stations may also have some effect on the higher ethane levels in Tokyo than in the suburban area.

[32] When considering the production of photochemical oxidants and SPM, the effect of NMHCs depends largely on the reactivity of the compounds. Very reactive NMHCs decompose rapidly after their emission, making it difficult to monitor these compounds and estimate their emissions from observational data. The compounds discussed in detail in this paper are generally rather stable, so that they can be easily measured and analyzed, but the results can be applied to estimate the emissions of other reactive compounds from common sources. In the case of Komaba and Kisai in the summertime, the main sources of C_2 – C_7 NMHCs were automobiles (both from tailpipes and from fuel tanks), solvent use (individual-scale to industrial-scale), and the leakage of LPG or LNG. The results of this study show the considerable effect of automobile emissions at both urban and suburban sites; signals of considerably high toluene emissions from small-scale manufacturers and some LPG leakage at Kisai. We did not quantitatively compare the levels of isoprene between Komaba and Kisai but suburbs are generally richer in vegetation than cities so that the emission of this very reactive compound can be highly elevated in suburbs and can therefore greatly affect local air quality under high NO_x conditions [Guenther *et al.*, 1993]. These results indicate that, depending on the structure of local industries, the number of vehicles, the proportion of vehicle types, and the biogenic NMHC emissions, the effect of pollutants can be comparable or even worse in the suburbs than in the central city. In order to control local air quality in the suburbs, continuous monitoring of the chemical composition of the local air is very important, as well as the promotion of lower emission vehicles and the regulation of stationary source emissions.

4. Conclusions

[33] The ambient atmospheric concentrations of eighteen C_2 – C_7 NMHCs (7 alkanes, 8 alkenes, 1 alkyne, and 2 aromatics) were measured hourly during the IMPACT measurement campaigns conducted in central Tokyo in four different periods from 2003 to 2004, and in the suburbs of Tokyo in 2004. Both diurnal and seasonal variations of the measured trace gas mixing ratios were significantly affected by wind speed, mixing height, land sea breeze circulation and mesoscale weather conditions. Isoprene showed a distinct diurnal variation in the summer. The mixing ratio of isoprene tightly correlated with solar flux and tempera-

ture measured at the observation site ($r^2 = 0.7$ and 0.5 , respectively), indicating local vegetation as its dominant source. In autumn and winter, no such correlation was observed and the atmospheric level of isoprene (0.02 ± 0.08 ppbv) was 10 times lower than in summer (0.27 ± 0.36 ppbv).

[34] For the majority of the measured NMHCs, the maximum mixing ratios were observed in winter. This can be explained by the low levels of OH radical and the lower mixing height in the winter. However, the winter maximum was not clear for C_4 – C_5 alkanes and *n*-hexane. For these species, the increase of temperature-dependent evaporative sources was indicated by comparing the correlations among the measured NMHCs between the summer and winter data sets. In winter, all of the observed NMHCs showed very tight correlations with each other, with the exception of isoprene. The correlations were fairly good both with CO and ethyne ($r^2 > 0.53$), which are considered to be emitted mostly from automobiles in urban areas, suggesting that car exhaust was the major source of C_2 – C_7 NMHCs in central Tokyo in the winter. Using the tight correlations of NMHCs with ethyne, a typical chemical composition of measured NMHCs in winter urban air was derived and compared with the chemical compositions in the plumes observed in the summer. Using also the previously measured source profiles, the results indicate a summer increase of C_4 – C_5 alkanes from fuel evaporation; of C_2 – C_3 alkenes, *n*-hexane and benzene from the chemical industry; and of toluene from local manufacturers, reflecting the temperature dependence of these evaporative emissions. As most of the evaporative sources are NO_x -free, these extra emissions from evaporative sources and increased emissions of terpenes from vegetation sources may increase the NMHC/ NO_x ratio, and thus enhance the production of photochemical oxidants on hot summer days.

[35] The observed average ambient concentrations of light NMHCs in the suburban area were comparable to central Tokyo in the summer in 2004, showing the potential of large emissions in suburban areas depending on the level of industrial activities and of regulations in each area. In the case of the Kisai observation site, toluene had a significantly higher concentration, which can be explained by the substantial emissions from local industries reported by the prefecture. In response to the recent expansion of areas affected by high-level photochemical oxidants, it is important to monitor and control NMHC emissions in suburban areas as well.

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